Using Noble Gas and Hydrocarbon Gas Geochemistry to Source the Origin of Fluids in the Eagle Ford Shale of Texas, USA

Undergraduate Research Thesis

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by

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Abstract

The Eagle Ford Shale in south Texas has become one of the most prolific shale plays in the United States in recent years. While production data suggests that oil and natural gas can be produced across a vast area of the field, the source of H_2S and hydrocarbons, and the extent to which fluids have migrated into and out of the Eagle Ford, have yet to be determined. This study uses noble gas isotopes, gas composition, and stable isotopes to evaluate the source gases, to characterize the fluids-in-place, and to characterize the extent of fluid migration from the Eagle Ford Shale.

The inert nature and distinct isotopic compositions make noble gases ideal tracers of crustal fluid processes. New data from the Eagle Ford presented herein show that mantle-derived gases (elevated $^{3}He/^{4}He$= 0.15-0.25Ra and $^{20}Ne/^{22}Ne$=10.2-11.1) and radiogenic gases (^{4}He, ^{21}Ne, ^{40}Ar) dominate the overall gas composition. Volcanism during Cretaceous/Cenozoic rifting activity probably caused the observed mantle-gas contributions. Interestingly, higher mantle contributions appear to correlate with elevated H_2S in the production wells from this study suggesting thermal sulfate reduction induced by magmatic activity.

Additionally, ASW and radiogenic noble gases can be used to model the relative volume of residual fluids-in-place for this Eagle Ford play. Data suggest that there has been minimal fractionation of noble gases implying minimal loss of the initial hydrocarbon fluids.

1. Introduction

Noble gas geochemistry provides a suite of geochemical tracers that can constrain the source and influences of various physical processes of fluid migration and fluid-rock interactions in Earth's crust and mantle (Ballentine et al, 2002). Although biomarker geochemistry, hydrocarbon gas compositions, and stable isotopes are traditionally applied for geochemical investigations of petroliferous basins, there are, in some cases, important applications for novel noble gases applications in hydrocarbon systems that provide information otherwise unobtainable by traditional techniques.

The onset of unconventional drilling has provided us with access to new types of samples, specifically from black shale hydrocarbon source rocks, that can be used to more broadly constrain the geology of a specific region. More importantly, unconventional drilling provides access to fluid samples previously unstudied due to the trap and seal nature of shale rocks. In applying noble gas geochemical techniques, we will be able to determine if fluids currently present in low permeability formations are remnant of depositional, diagenetic, and catagenetic processes or if they have migrated from other sources, such as the mantle or another shale deeper in the stratigraphic column.

Because of their inert nature and well characterized source and isotopic attributes, noble gases are not altered by the many chemical reactions (e.g., chemical oxidation, reduction, or hydrocarbon "cracking") that occur throughout processes such as organic carbon deposition, diagenesis, catagenesis, or water-rock interactions that occur during hydrocarbon migration (Sherwood Lollar and Ballentine, 2009). Noble gases allow workers to investigate the evolution of sedimentary basins and tectonic plate margins, distinguish between crustal and mantle-derived

fluids, and characterize the style, extent, and degree of migration of petroleum or other crustal fluids (Ballentine et al, 1991; Hunt et al 2012).

The Eagle Ford Shale of south Texas has, arguably, been one of the greatest success stories associated with unconventional energy development in US or abroad. Unconventional energy extraction involves the combination of horizontal drilling and hydraulic fracturing, which has dominated onshore petroleum production throughout much of the last decade and is poised to make the US a net exporter of petroleum by the year 2020 (Vengosh et al, 2014). For example, from January through October of 2014, the Eagle Ford Shale produced more than 955,000 barrels of oil per day and more than 4,600 million cubic feet of wet natural gas per day (Texas Railroad Commission, 2014). The term wet gas is used because the C_2+/C_1 exceeds 0.05 (i.e., more than 5% ethane or heavier aliphatic hydrocarbons).

When exploring the Eagle Ford shale, the petroleum industry has well constrained spatial information about the thermal maturity of the formation in terms of oil-prone and gas-prone, specifically wet gas regions (Texas Railroad Commission, 2014). However, there is still significant local variation in oil and gas production due to the complex tectonic and associated structural history of the region coupled with local, but variable thermal influences and variable quality and economic values of produced gases.

An additional aspect of hydrocarbon production in the Eagle Ford that has troubled production is the seemingly-random presence of highly elevated hydrogen sulfide gas (H_2S) concentrations. Hydrogen sulfide gas concentrations vary greatly from one well to others in close proximity, and deadly concentrations have been reported in some areas in the Eagle Ford. Three main processes can lead to the production of H_2S in various geologic settings including: 1)

migration of the gas from an external source; 2) bacterial sulfate reduction (BSR), and 3) thermochemical sulfate reduction (TSR).

One potential external source that would lead to the migration of H_2S in this region is nearby volcanism and associated geothermal systems, the nature of which is discussed in the geologic background section of this study. Nonetheless, regional groundwater flow through reducing aquifers cannot be excluded *a priori* (Machel, 2001). While BSR can be a major source of H_2S generation in many shallow aquifers and other hydrocarbon reservoirs, this process rarely occurs above 80°C (Machel, 2001). Because oil generation does not begin until approximately the same temperature (~80°C), the production of H_2S by BSR is unlikely to continue to occur today, but could have conceivably occurred before the basins achieved sufficient thermal maturity for petroleum catagenesis. TSR is feasible when organic reactants (e.g., petroleum), sulfate, and temperatures exceeding 100°C, which serves as the catalyst, occur contemporaneously (Machel, 2001). We will examine the viability of these processes below.

In order to characterize hydrocarbons from the Eagle Ford Shale and examine the source and migration of hydrocarbons and H_2S, we have collected and analyzed samples from actively producing commercial wells in the Eagle Ford; our data and interpretation will be used to provide insights into the many geologic interactions that have influenced the region and its oil and gas compositions. The consequences of these connections lead to an understanding of the multiple sources of fluids in the Eagle Ford Shale, with a particular influence on mantle-derived contributions, and a model for predicting the abundance of H_2S.

2. Objectives

The overall goal of this research project is to use noble gas geochemistry to determine the geologic history and hydrocarbon production. The necessary steps are as follows:

- To establish a robust suite of oil and gas samples that have associated production data in the Eagle Ford area
- To analyze each sample for major and hydrocarbon gas composition
- To analyze each sample for noble gas composition and isotopes
- To identify any mantle-derived contributions to the fluids in the Eagle Ford Shale
- To find the relationship between normal faults and fluid composition
- To fingerprint the source of hydrogen sulfide (H_2S) gas present in the Eagle Ford
- To find a correlation between total available hydrocarbon production and noble gas geochemistry

3. Background

3.1 Geological Background

The study area is located in Eagle Ford Shale in Atasocsa, Frio, and Lasalle Counties in southern Texas, USA. Regionally, this area is east of the Maverick Basin and west of the San Marcos Arch (Figure 1). The Eagle Ford Shale is different from many traditionally exploited petroleum systems in that there are several major tectono-structural features that have influenced its progression through geologic time.

Underlying the Eagle Ford, the Buda Limestone is a thick, micritic wackestone (Treadgold et al, 2010). The Eagle Ford Shale is an Upper Cretaceous organic-rich shale that is commonly divided into two members: a lower, organic-rich mudstone and an upper, more calcareous mudstone with lower organic content. Between these two shale members lies a thin carbonate known as the Kamp Ranch Limestone (Treadgold et al, 2010). In looking at the stratigraphic column of south Texas (Donovan and Staerker, 2010), the Eagle Ford is the last shale deposited in a deep water setting preceding basin-filling deposition that includes two distinct limestones that eventually transition into a series of clastic deposition in the Tertiary. Unconformably overlying the Eagle Ford is the well-known Austin Chalk, which is another thick limestone (Treadgold et al, 2010). In well logs, these surrounding limestones have much lower gamma ray readings (a proxy for organic carbon content) than the organic-rich shales in between. The lower member of the Eagle Ford has a notably higher gamma ray reading than the upper member due to the higher organic content (and associated U) and more frequent, thin bentonite (an ash of volcanic clay) beds (Denne et al, 2014).

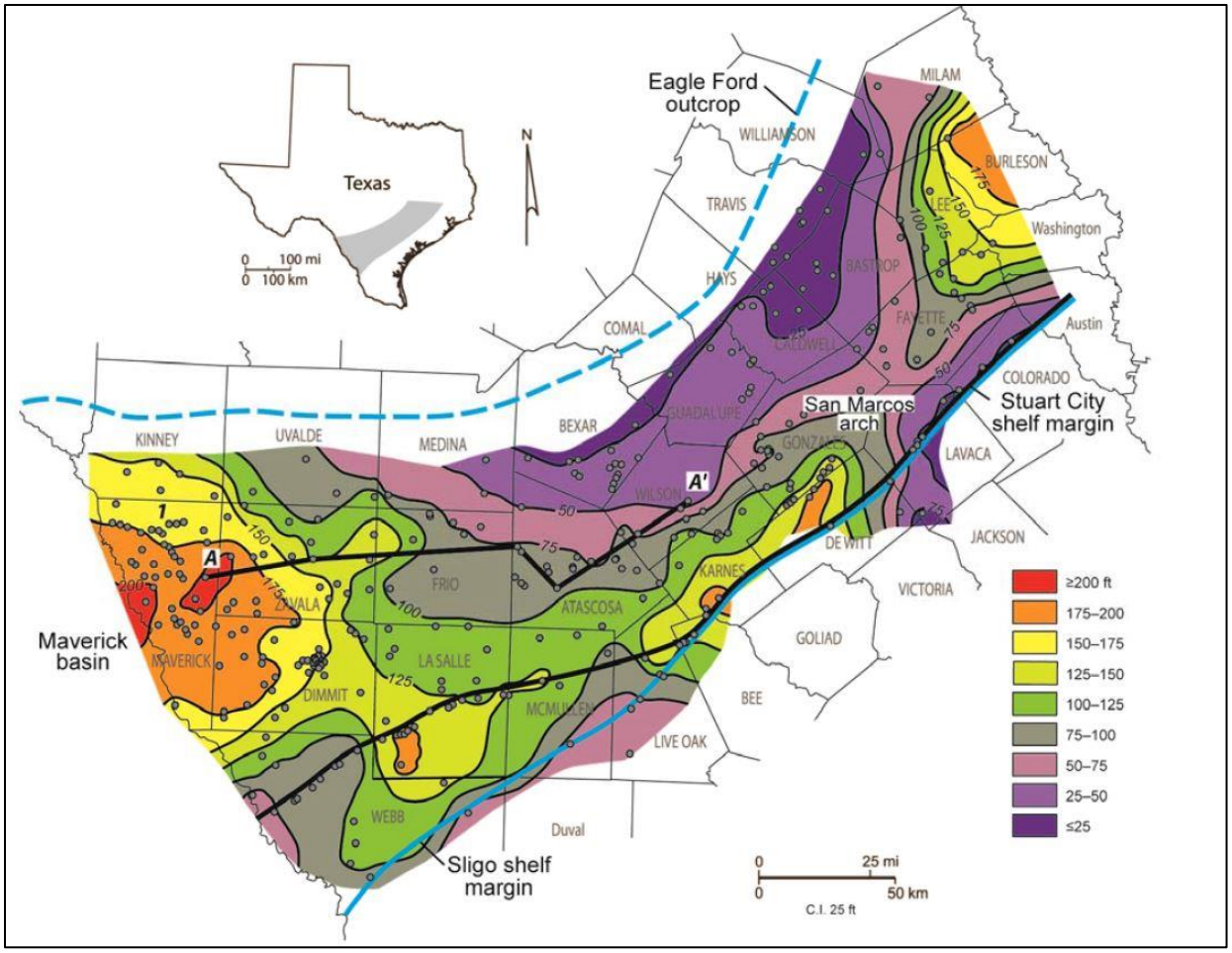


Figure 1. Isopach map of the Eagle Ford Shale in south Texas with major, regional structural features (Hentz et al, 2014).

The Eagle Ford Shale is traditionally interpreted as having been deposited in a deep-water environment (Treadgold et al, 2010), as is assumed for many economic black shales globally. The deposition of the Eagle Ford Shale is thought to have occurred when the Cretaceous Interior Seaway merged into the still-forming Gulf of Mexico in the region. Denne et al (2014) divide the deposition of the Eagle Ford into a western, carbonate-dominated setting and an eastern, clastic-dominated setting, with the San Marcos Arch as the dividing line.

After Ewing (1987), the major contributing structural factors, not in temporal order, in the Eagle Ford are: 1) the convergent salt tectonics of the Gulf Coast region in which the Louann Salt formation functioned as a regional decollement for the superior thrust sheet; 2) extension

that led to normal faulting which began in the Jurassic and continued at least through the Eocene; 3) subsequent basaltic intrusions associated with Cretaceous rifting and volcanism, and 4) Laramide compression.

In terms of piecing together timing and causes of fluid movement, the combination of these influences creates much difficulty. The Louann Salt, a major player in petroleum development across much of southeast Texas, Louisiana, and the Gulf of Mexico, is present but pinches out near the study area, close in proximity to where normal faulting begins and takes over northward (Ewing, 1987). By the time the Eagle Ford was deposited, however, the dramatic effects of the resulting salt tectonics had dissipated (Pearson et al, 2012). As a result, we will not further detail the regional effects of this feature.

Laramide folds extend to the western extent of the Eagle Ford's presence in southwestern Texas, but likely do not have significant impact on our study area. Clastic sediments derived from the Laramide orogeny helped form some formations overlying the Eagle Ford and Austin Chalk well after Eagle Ford deposition, and likely contributed to burial, and hence thermal maturation, of the Eagle Ford Shale itself. One major Laramide fold, named the Chittim Anticline, is located just to the northwest of the sampling area (Ewing, 1987). The timing of this feature had a significant impact on the maximum burial depth that the Eagle Ford reached, as hydrocarbons along the hinge of the anticline have a much lower thermal maturity than those on either side of it (Cabot proprietary documents, 2014).

The most prominent structural features in this region include normal faults, which strike through our current study area. Three main fault systems (Figure 2) strike from the southwest to the northeast and are, from north to south respectively, the Balcones Fault Belt, the Luling Fault Belt, and the Charlotte Fault Belt (sometimes called the Charlotte-Jourdanton Fault Belt)

(Fowler, 1956). We will omit discussion of the Balcones and Luling Fault Belts for brevity and remoteness in regards to the study area. The Charlotte Fault Belt directly affects the geology of the study area, and notably contains a sharp southward bend in southern Frio County. Normal faulting in this system began during the deposition of the Eagle Ford time and continued through the Tertiary (Fowler, 1956). Crustal thinning associated with the normal faulting led to igneous activity across much of south Texas (Ewing, 1987).

Throughout the region, the occurrence of normal faults is associated with volcanism, which is located primarily to the northwest of the study area in Zavala County. The igneous activity in the area is found in a series of discrete basalt edifice volcanoes and fissural basalt flows that later underwent serpentinization. Fowler (1956) notes that the volcanic edifices did not occur with any spatial relevance to the fault belts near our study area, but were contemporaneous with fault propagation. Alteration of basaltic flows produced localized serpentinite deposits, which have been observed in Eagle Ford core samples although the spatial occurrence of these deposits are not regionally continuous and cannot be correlated on regional scales. These volcanics were ultramafic, silica-undersaturated, and highly alkaline, and have been compared to rocks in the East African Rift (Ewing et al, 1982; Chakrabarti et al., 2009; Tedesco et al., 2010).

The three main fault zones mentioned above give rise to the notion that rifting may have initiated, but did not progress to any great extent in this region as there is no evidence of active rifting during this time (Ewing et al, 1982). This allows an investigation of fluids in what is likely a failed rift system, which is not easily explored in many geological settings. The faults, igneous activity, and associated increase in crustal heat all may play important roles in the sources, composition, and migration of fluids found in the Eagle Ford and can provide important insights on fluids in other failed rift settings. It is crucial to characterize these local heat sources

in order to understand the impacts of thermal maturation and, in particular, evaluate the potential for thermochemical sulfate reduction as a source for H_2S in this area.

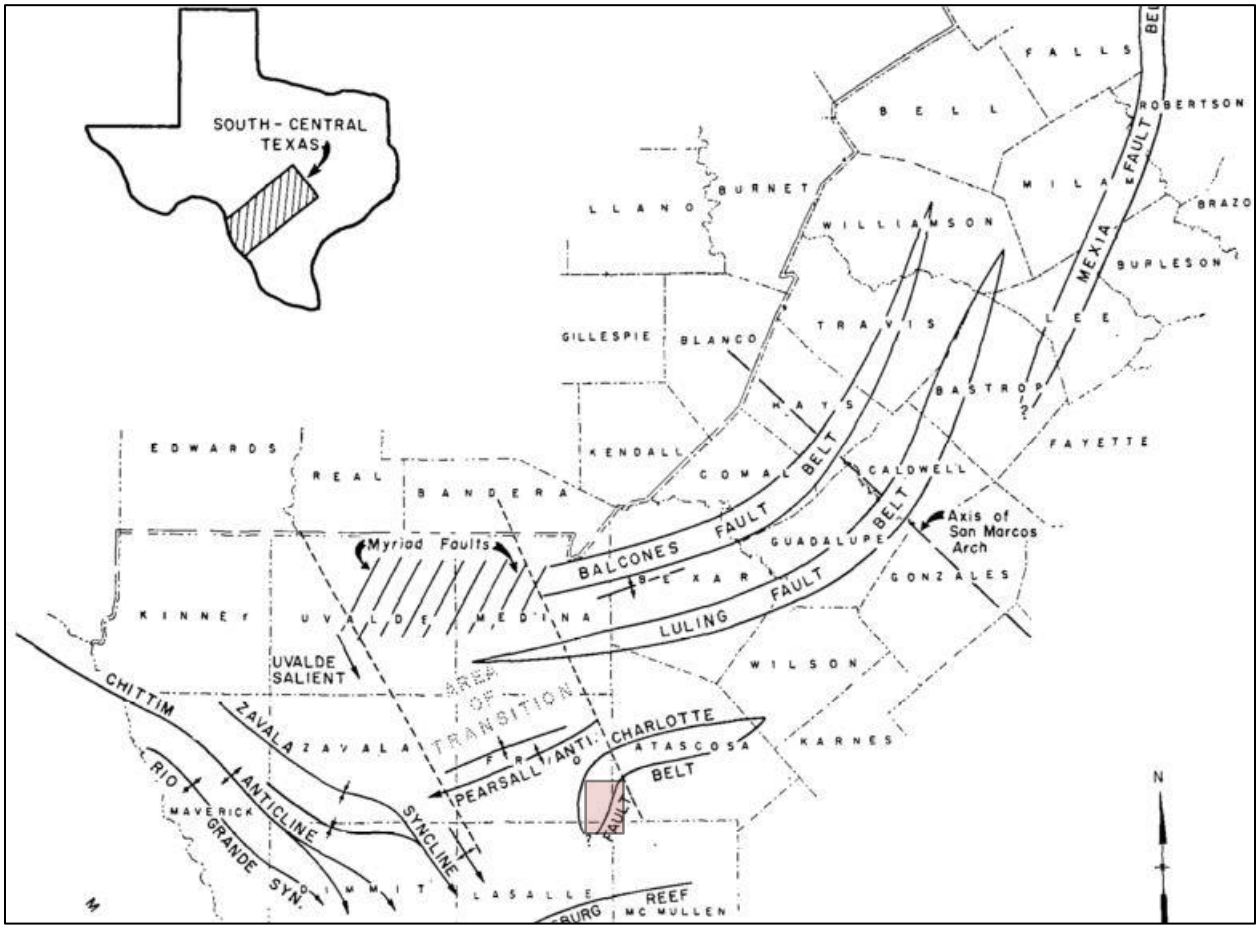


Figure 2. Map of tectonic features in south Texas. Our study area is represented by the pink box. Notice the three parallel fault belts within and north of the study area (Fowler, 1956).

The current study will evaluate 27 samples collected from commercial producing oil and gas wells in Atascosa, Frio, and Lasalle Counties in the state of Texas, USA. Each sample was analyzed for major gas composition (methane (CH_4 or C_1), ethane (C_2), propane (C_3), butane (C_4), pentane (C_5), hydrogen (H_2), carbon dioxide (CO_2), nitrogen (N_2)), noble gas isotopic composition (He, Ne, Ar, Kr, Xe and their isotopes), and stable isotopic composition of carbon dioxide and compound-specific of hydrocarbon gases (C_1 to C_5).

3.2 Geochemical Background

Noble gases are valuable geochemical tracers because of their inert nature. They are unaltered by chemical or biological processes (e.g., bacterial reduction, oxidation)), have low natural abundance, and exhibit predictable behavior in various fluids (Ballentine et al, 1991; Darrah et al, 2013; Darrah et al, 2014;). As a result, their original composition is preserved in crustal fluids independent of microbial activity or changes in oxygen fugacity. The well-characterized isotopic composition of major terrestrial reservoirs (i.e., mantle, crust, hydrosphere, and atmosphere) and coherent physico-chemical response to changing fluid conditions make noble gases uniquely valuable for constraining the source, mixing, mechanism of transport, and residence time of crustal fluid. Specifically, each of the noble gases has a uniquely different solubility and diffusional constant in various types of fluids (e.g., water, oil, gas). As a result, each of the noble gas isotopes is predictably fractionated by known physical processes such as single-phase advection, multiple-phase advection, and diffusion.

While there is a paucity of noble gas data available in oils, and no previous noble gas data available in the present study area, atmospheric, crustal, and mantle noble gas compositions are well studied in a variety of fluids. The air-saturated water (ASW) composition of groundwater is constant globally for both concentration and isotopic composition. As a result, the concentrations of ASW components in crustal water are a well-constrained function of temperature, salinity, and atmospheric pressure (elevation). Atmospheric noble gases (AIR) dissolve in groundwater when meteoric water equilibrates with the atmosphere prior to recharge into the subsurface. This equilibration follows Henry's Law, with solubility increasing with higher atomic mass: He<Ne<Ar<Kr<Xe (Weiss 1971a, Weiss 1971b).

Shallow groundwaters typically have ASW noble gas composition characterized by near solubility levels of [^{4}He] (~40-45 x 10^{-6} cm^3 STP/L), [Ne] (175-220 x 10^{-6} cm^3 STP/L), and [Ar] (0.28-0.49 cm^3 STP/L). Isotopically each gas component is similar to atmospheric compositions (i.e., helium: ^{3}He/^{4}He=1.36 x 10^{-6} or ~0.985*Ra* where *Ra* is the ratio of a sample relative to AIR= 1.39 x 10^{-6}); neon: ^{20}Ne/^{22}Ne (~9.8) and ^{21}Ne/^{22}Ne (~0.0289); and argon: ^{38}Ar/^{36}Ar (~0.188) and ^{40}Ar/^{36}Ar (~295.5). With the exception of helium (0.985*Ra*), the isotopic effect related to Henry's Law solubility dissolution into meteoric water is less than the measurement error for Ne and Ar.

The second major source of noble gases in crustal fluids includes the isotopes produced *in-situ* by radioactive decay. As hydrocarbon or meteoritic fluids interact with crustal fluids, the noble gas composition changes through the radiogenic nature and geologic history of the rocks through which fluids migrate within the Earth's crust (i.e., termed crustal gases). Crustal gases are produced from the decay of ^{235}U,^{238}U, ^{232}Th (^{4}He* (α-decay) and ^{21}Ne* (α-n reactions) and K (^{40}Ar* (electron capture)) at known decay rates. Marine sediments, such as black shales, are typically enriched in uranium content (specifically in comparison to thorium) as a result of uranium adsorption onto organic-rich particles during sediment deposition. In black shales, the typical range of concentrations are: uranium (~1-30 ppm), thorium (~1-30 ppm), and ^{40}K (total K~26,000 ppm, with a [^{40}K] /K ratio of 1.170 x 10^{-4} = ~3 ppm of ^{40}K of which 11% decays to ^{40}Ar*) (Taylor and McLennan 1995). This radioactive decay leads to characteristic ratios of these radiogenic gases in crustal rocks such as thermally mature black shales (Hunt et al. 2012). Typical isotopic ratios of crustal noble gases are ^{3}He/^{4}He= ~0.01Ra, ^{20}Ne/^{22}Ne (~9.7-10.0), ^{21}Ne/^{22}Ne (~0.029-0.060), and ^{40}Ar/^{36}Ar (~295.5-1100)), respectively (Darrah et al, 2013; Ballentine et al, 1991).

Once radiogenic gases are formed in the crust, they are released from different lithologies at predictable and quantifiable rates as a function of formation temperature (i.e., release correlates to thermal maturity) (Hunt et al, 2012; Ballentine et al, 1991; Darrah et al, 2014). Because of its small atomic radius, helium can diffuse through quartz on geologic time scales as short as decades, particularly at the elevated temperatures of hydrocarbon formations, and thus equilibrate with crustal fluids. Compared to heavier noble gases, helium is preferentially released from mineral grains in the crust. In general, helium ($^{4}He^{*}$) content is higher in older formations and uranium-rich formations (e.g., black shales). Following catagenesis and metagenesis (conversion of organic kerogen to oil and then gas), helium is further enriched in hydrocarbon gases or other crustal fluids (water or oil) that experience significant migration. The processes that enrich helium in migrating fluids result from the relatively lower solubility (higher partition coefficients) and high diffusivity of helium as compared to methane or heavier noble gases in crustal fluids. In comparison to ^{4}He, radiogenic ^{40}Ar ($^{40}Ar^{*}$) is only released from crustal mineral grains into migrating fluids at higher temperatures (~220^{o}C) if K-rich feldspars present in crustal detritus break down, or if K resides within exchangeable sites (i.e., clays). As a result, the relative $^{4}He/^{40}Ar^{*}$ ratio is a sensitive marker for temperature-dependent release history of thermogenic hydrocarbon gas.

The third component that is found in some crustal settings is primordial noble gases. Primordial gases are derived from meteoritic and cosmogenic sources during the formation of the planet, and today are found in the mantle-derived rocks and fluids (Lupton and Craig, 1975; Ballentine et al, 2002). The most common example of primordial gas is ^{3}He (Ballentine et al, 2002).

Once incorporated into crustal fluids, isotopic fractionation of noble gases from any of these source occurs during some aspect of fluid migration (e.g., advection, diffusion).

4. Methods

4.1 Sample Selection

We analyzed the noble gas isotopic composition of oil and associated gases of 27 horizontally-drilled and hydraulically fractured oil wells actively producing in Frio, Atascosa, and LaSalle Counties, Texas in conjunction with Cabot Oil and Gas. This area is located near the Charlotte-Jourdanton Fault Belt and underlain by the Eagle Ford Shale. The typical depth of the Eagle Ford in these wells ranges from 5000 ft (1524m) to 8000 ft (2438m). We integrate our noble gas and hydrocarbon gas data with production data (first oil date, total gas produced, total oil produced, and total water produced) and proximity to fault-related features provided for each well.

4.2 Sampling and Analysis

All oil and associated gas samples were analyzed for their major gas abundance (e.g., CH_4, C_2H_6, H_2S, O_2), noble gas composition (He, Ne, Ar, Kr, Xe and their isotopes), and stable carbon isotopic composition (reported elsewhere) according to standard analytical methods (Hunt et al, 2012; Darrah et al, 2013; Darrah et al, 2014). Before sampling, we ensured wells had been in continuously active production to confirm that no stagnant fluids were obtained. Samples were collected from a production line adjacent to the wellhead.

The oil and associated gas samples were collected in refrigeration-grade copper tubes that were flushed with at least 50 volumes of sample fluid before crimping or sealing with stainless steel clamps. In the laboratory, the fluid was extracted from the copper tube on a vacuum line and sonicated for ~30 minutes to ensure the total transfer of dissolved gases from the comingled fluid into the sample inlet line (Solomon et al, 1995; Pinti and Marty, 1995).

Major gas components (i.e., CH_4, C_2H_6, N_2, CO_2, H_2, O_2, Ar) were measured using an SRS quadrupole MS at The Ohio State University. All samples were analyzed in triplicate. Standard analytical errors were all less than ± 3.3% for major gas concentrations above the detection limit. Daily values based on "known-unknown" analyses of external precisions standards are reported in the parentheses - CH_4 (0.95%), C_2H_6 (0.95%), N_2 (1.25%), CO_2 (1.5%), H_2 (3.3%), O_2 (2.1%), Ar (0.95%) - as determined by measuring referenced and cross-validated laboratory standards including a) an atmospheric standard (Columbus Air) and b) a synthetic natural gas obtained from Praxair.

The isotopic analyses of noble gases were performed using a Thermo Fisher Helix SFT MS at The Ohio State University Rare Gas Facility. All samples were analyzed in triplicate. Standard analytical errors were all less than ± 3.1% for noble gas concentrations with daily values reported in parentheses - [^{4}He] (0.8%), [^{22}Ne] (1.1%), [^{40}Ar] (0.2%), [^{84}Kr] (1.6%), [^{132}Xe] (3.1%) - as determined by measuring referenced and cross-validated laboratory standards including a) an established atmospheric standard (Columbus Air) and b) a synthetic natural gas obtained from Praxair including known and validated concentrations of C_1 to C_5 hydrocarbon, N_2, CO_2, H_2, O_2, and each of the noble gases. Noble gas isotopic errors were approximately ±0.01 times the ratio of air (or 1.4 x10^{-8}) for ^{3}He/^{4}He ratio, less than ±0.49% and less than ±0.91% for ^{20}Ne/^{22}Ne and ^{21}Ne/^{22}Ne, respectively, less than ±0.85% for ^{38}Ar/^{36}Ar and ^{40}Ar/^{36}Ar, respectively (higher than typical because of interferences from C_3H_8 on mass=36 and 38), less than ±1.90% for ^{82}Kr/^{84}Kr, and less than ±1.4% for ^{130}Xe/^{132}Xe. The helium (^{3}He/^{4}He) isotope ratio is hereafter expressed as R/Ra ratios where R is the measured ratio and Ra is the ^{3}He/^{4}He of air (1.39x10^{-6}) (Pepin and Porcelli, 2002).

5. Results

The data in figures below are from the 27 samples analyzed without any obvious air contamination. For notable major gas chemistry components, CH_4 concentrations ranges from 0.116 to 0.672 ccSTP/cc, C_2H_6 ranges from 0.0819 to 0.338 ccSTP/cc, CO_2 ranges from 0.0174 to 0.159 ccSTP/cc, and H_2S ranges from 14.7 to 4980 µccSTP/cc (ppm). The ^{3}He concentrations ranges from 0.024 to 25.1 pccSTP/cc (parts per trillion), ^{4}He concentrations ranges from 0.128 to 111 µccSTP/cc (ppm), ^{20}Ne ranges from 0.0028 to 0.152 µccSTP/cc (ppm), ^{36}Ar ranges from 1.72 to 10.6 µccSTP/cc, ^{40}Ar ranges from 1050 to 8170 µccSTP/cc (ppm), ^{84}Kr ranges from 84.7 to 1110 nccSTP/cc (ppb), and ^{132}Xe ranges from 18.6 to 359 nccSTP/cc (ppb).

Ratios of particular major gas and noble gas components were calculated for each well. The Eagle Ford Shale contains wet hydrocarbon gas (C_2+/C_1= 0.11 to 1.4) that is consistent with oil-associated gas during early petroleum generation. The range of $\delta^{13}C$-CH_4 is -48.3 to -35.5 per mil and the range of $\delta^{13}C$-C_2H_6 is -36.7 to -33.9 per mil. The range of $\delta^{13}C$-CO_2 is -10 to -1 per mil. The helium isotopic composition is shown as R/Ra, where R is the absolute ratio of $^{3}He/^{4}He$ in a sample and Ra is the absolute ratio of $^{3}He/^{4}He$ in air ($1.39x10^{-6}$). In our current sample set, R/Ra values range from 0.0973 to 0.207, which range up to almost 20x higher than the helium isotope composition of average crustal rock (~0.01R/Ra) (Ballentine and Burnard, 2002).

6. Discussion

6.1 Hydrocarbon Gas Composition

All 27 samples collected as part of this study are consistent with early maturity natural gases (Schoell, 1980; 1983) commonly associated with petroleum liquids (i.e., these are consistent with archetypal "oil associated gases") (Jenden et al, 1993). Classically, natural gases such as these are termed wet gas because the C_2+/C_1 exceeds 0.05 (i.e., more than 5% ethane or heavier aliphatic hydrocarbons). In our dataset, we observed exceptionally high values of C_2+/C_1 that range from 0.11 to 1.4 (i.e., more C_2+ than C_1 in many samples), ratios that are uncommonly observed in many geological settings. The high concentrations of ethane and higher aliphatic hydrocarbons suggest a clear thermogenic origin of the natural gas.

The $\delta^{13}C\text{-}CH_4$ for our samples ranges from -48 to -36 per mil, which are also consistent with thermogenic hydrocarbon gases. By comparison, microbes, like all living organisms, prefer ^{12}C to ^{13}C and typically produce a much lighter $\delta^{13}C\text{-}CH_4$ (~ -70 per mil). Consistent with a thermogenic source of these gases, the $\delta^{13}C\text{-}C_2H_6$ ranges from -36.7 to -33.9 per mil. For any individual sample, the $\delta^{13}C$ of C_2H_6 is greater than the $\delta^{13}C$ of CH_4, which is consistent with an early thermogenic stage of gas generation.

Gas compositions so rich in non-methane aliphatic hydrocarbons are either the result of the earliest generation of gas-phase hydrocarbons from the cracking of liquid petroleum or the earliest ordering of kerogen following thermal maturation. While future work will be required to determine the maturity of hydrocarbon by using compound-specific stable isotopes in hopes of differentiating between the two possibilities, it is important to note that these samples represent some of the earliest maturity hydrocarbon gases yet reported.

6.2 Source of Carbon Dioxide

One peculiar aspect of oil-associated gases from the Eagle Ford Shale is the consistent presence of carbon dioxide. Carbon dioxide is a common component in many fluids in a diverse set of Earth's systems, which can be derived from the following hypotheses: a) thermal alteration of marine carbonate minerals; b) microbial oxidation of petroleum or organic carbon; or c) migration of externally-sourced mantle-derived fluids.

Stable isotopes of carbon dioxide are commonly used to determine the source of CO_2. Atmospheric CO_2 has a $\delta^{13}C\text{-}CO_2$ value of -8 per mil, which leads to air-saturated water with a $\delta^{13}C\text{-}CO_2$ value of ~0 (-2 to +2) per mil consistent with values observed in marine carbonate minerals (Craig, 1953). Microbial CO_2 derived from the oxidation of plant matter yields $\delta^{13}C\text{-}CO_2$ ranging between -26 to -22 per mil in rocks deposited before the Miocene (Cerling and Quade, 1992). Similarly, the oxidation of petroleum or kerogen *in situ* yields $\delta^{13}C\text{-}CO_2$ that ranges from -26 to -16 per mil on average (Prinzhofer and Huc, 1995). By comparison, exogenous mantle carbon can also make its way into hydrocarbon reservoirs or shallow subsurface, through multiple avenues (e.g., crustal emplacement of volcanic products or fluid migration along regional fault sets). Kimberlite pipes bring up carbon typically in the form of diamonds, while geothermal areas are dominated by mantle-derived CO_2. Each of these sources has $\delta^{13}C\text{-}CO_2$ values from -10 to -2 per mil (Faure, 1986), which overlaps the total range of $\delta^{13}C\text{-}CO_2$ in our study.

$\delta^{13}C\text{-}CO_2$ values from our study range from approximately -10 to -1 per mil. This range is significantly heavier than one would expect for microbial inputs from either the oxidation of plant matter or liquid petroleum eliminating hypothesis b). Nonetheless, there is significant overlap between the $\delta^{13}C\text{-}CO_2$ ranges of sedimentary carbonates (hypothesis a) and mantle-

derived fluids (Poreda et al, 1988) (hypothesis c). Similarly, it is unclear if the lighter range of observed values may relate to a mixture of contributions from microbial components and another source, or if the lighter values may relate to isotopic fractionation during fluid migration/water-rock-gas interactions in the subsurface.

By combining $\delta^{13}C\text{-}CO_2$ with noble gas parameters one can provide further insights on the source of carbon dioxide and differentiate between hypotheses a and c. An important clue about the source of CO_2 comes from the helium isotopic composition of carbon dioxide gases. Average crustal rocks, as discussed in Section 5, have an R/Ra value of 0.01. The Eagle Ford Shale has R/Ra values an order of magnitude greater than the crustal production ratio, with an average of 0.13Ra. The elevated ^3He value we find most likely comes from mantle-derived gases that have migrated into the Eagle Ford Shale over geologic time. Evanzia et al (2014) suggest, via mantle tomography models, significant mantle anomalies across the entire state of Texas, including slow velocity anomalies, reflecting transport of melted fluids, beneath the Charlotte Fault Zone. Porritt et al, 2014, also model mantle tomography via USArray and discuss the slow velocity anomaly associated with the Rio Grande rift zone, as well as mapping slow anomalies beneath our study area. The elevated R/Ra is the last piece necessary to conclude the Charlotte Fault Zone represents a pathway that has received mantle-derived fluids.

Further evidence for the mantle contributions associated with the Eagle Ford samples are the R/Ra values in map-view (Figure 3). The higher values are clustered in a southwest to northeast trend, on the same strike as the Charlotte Fault Zone. Compared to the normal fault regime mapped using proprietary seismic data, this zone of increased ^3He falls directly in line with the grabens (dropdown blocks) of the failed rift. As a result, these normal faults associated with the downthrown grabens are likely the conduits by which mantle gas components migrated

upwards and become entrained in overlying units, likely along a failed rift margin. Potentially the low permeability shales associated with the Eagle Ford Shale act as a stratigraphic trap for migrated mantle-derived gases.

Similarly, the lower range of $CO_2/^3He$ values (approaching $2x10^9$) is also consistent with mantle sources (Ballentine et al. 2002; Gilfillan et al, 2009). By comparing the $CO_2/^3He$ vs. $\delta^{13}C$-CO_2, one can further interrogate the source of carbon dioxide (Figure 4). In this plot, one finds that the majority of samples plot along a two component mixture between mantle-derived fluids and a trend of increasing contributions from thermal alteration of carbonates (i.e., increasing CO_2 without additional ^3He) without a decrease in the $\delta^{13}C$-CO_2 (i.e., adding microbially-derived or organic CO_2) would lead to a lighter $\delta^{13}C$-CO_2 value. Together these observations preclude microbial alteration as a source of carbon dioxide and suggest that mantle-derived fluids are the more likely source of carbon dioxide.

We hypothesize that the most likely scenario that produced this trend is the injection of mantle-derived carbon dioxide at elevated temperatures (e.g., geothermal fluids) along normal faults that subsequently induced thermal metamorphism of existing sedimentary marine carbonates. Combined with the fact the Eagle Ford Shale is compositionally dominated by carbonate minerals, the consistency of $\delta^{13}C$-CO_2 with increasing $CO_2/^3He$ suggests that hydrothermal alteration may have occurred within the relatively homogeneous Eagle Ford Shale. The correlation between higher $CO_2/^3He$ and higher R/Ra (Figure 5) gives rise to the explanation that higher amounts of heat allow the increased alteration of carbonates, thus releasing progressively greater amounts of CO_2. There is a relative ^3He increase, indicating more heat from a mantle source, and an increase in CO_2 relative to ^3He, meaning the majority of CO_2 and ^3He do not share a common origin. This gas, however, is not the only one controlled by the mantle.

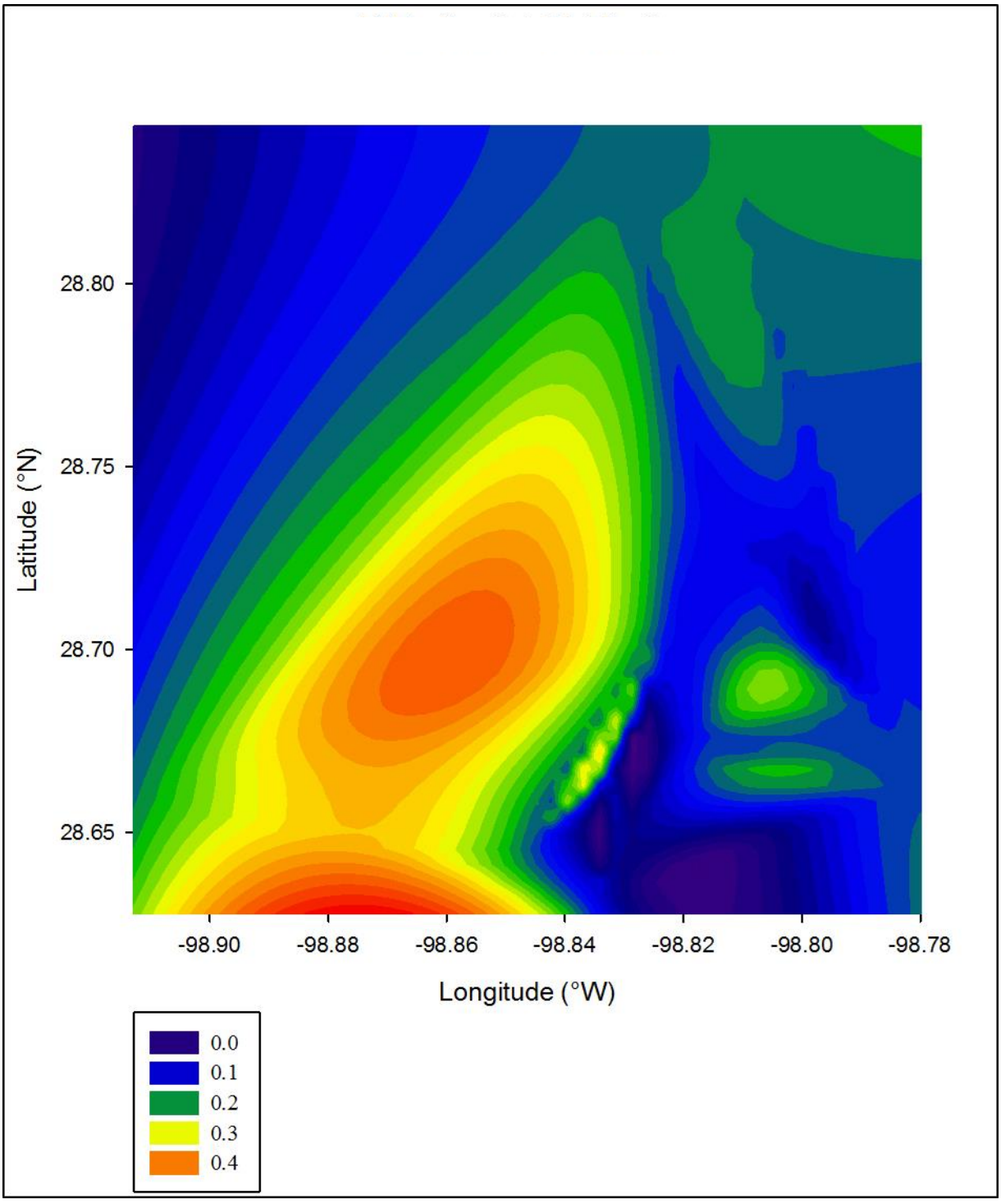


Figure 3. Colored contour map of R/Ra values in the study area. Elevated values follow a SW-NE trend, similar to the trend of the Charlotte Fault Zone. The highest values in the middle of the trend represent the down-dropped block of the normal fault system.

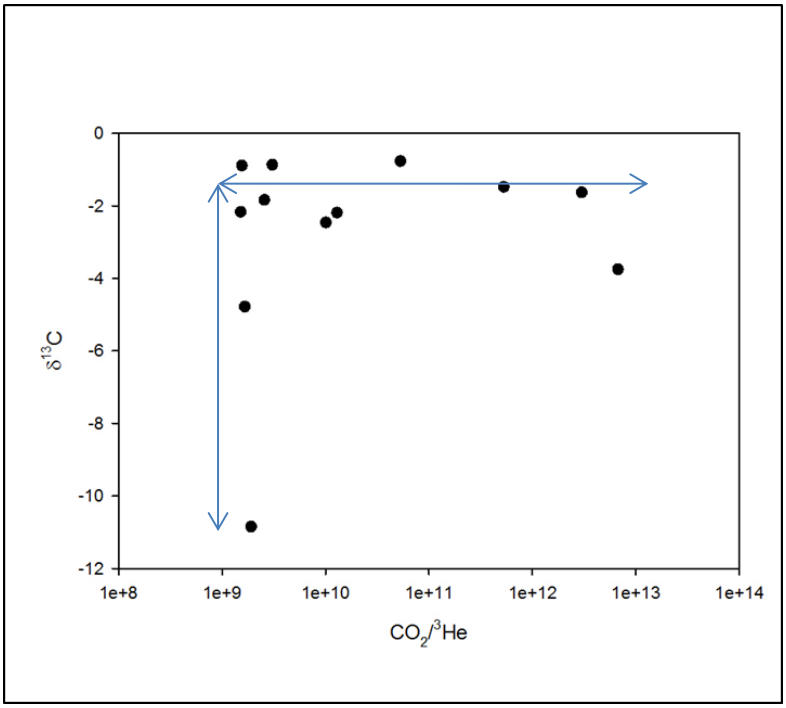


Figure 4. The $\delta^{13}C$-CO_2 vs $CO_2/^3He$. $\delta^{13}C$-CO_2 values remain fairly constant despite increasing $CO_2/^3He$. The variance in $\delta^{13}C$ values at 1e9 $CO_2/^3He$ represent the different sources of carbon dioxide in the system: mantle-derived CO_2 and marine carbonates. The horizontal arrow represents mantle mixing with carbonates while the vertical arrow could represent the addition of microbial Co_2

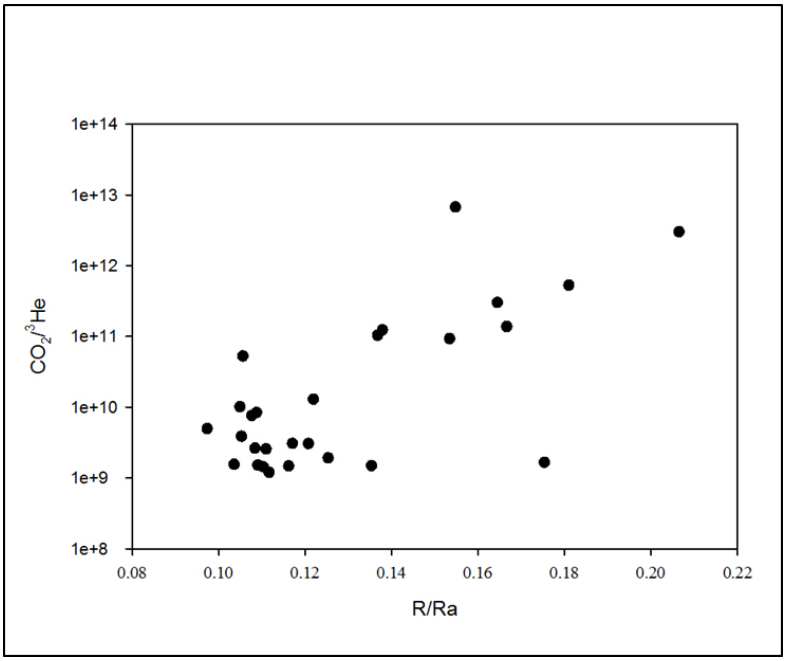


Figure 5. R/Ra vs $CO_2/^3He$. Increasing mantle contribution strongly correlates with elevated CO_2 relative to ^3He. Higher R/Ra represents increased thermal activity, leading to thermal alteration of marine carbonates, a very common Eagle Ford component.

6.3 H_2S

The presence of toxic H_2S is of great economic and environmental health and safety concerns to all those involved in the production of hydrocarbons in this region. H_2S gas is derived on the surface and in the subsurface of the Earth by two processes: bacterial sulfate reduction (BSR) and thermochemical sulfate reduction (TSR). Although H_2S is a common byproduct of oil and gas generation, temperatures for oil and natural gas generation typically exceed the range of temperatures at which sulfate-reducing bacteria can survive (Machel, 2001). At higher temperatures, TSR, which can occur at temperatures between 100° and 140°C, is often the more common mechanism for producing more H_2S.

Because of the unique noble gas and stable isotope tracers for external heat sources discussed above, we hypothesize that the associated isotopic tracers may be useful in distinguishing the source of H_2S, more specifically distinguishing between BSR and TSR. (Figures 6 and 7) Similar correlations exist between increasing H_2S concentration with increasing R/Ra and increasing $CO_2/^3He$, respectively. Combined, these plots indicate that H_2S is likely generated by the thermal alteration of marine carbonates. In essence, H_2S does not originate from the mantle, but TSR is activated by the increased temperatures as a result of the emplacement of hydrothermal fluids associated with volcanism and potentially the onset of rifting.

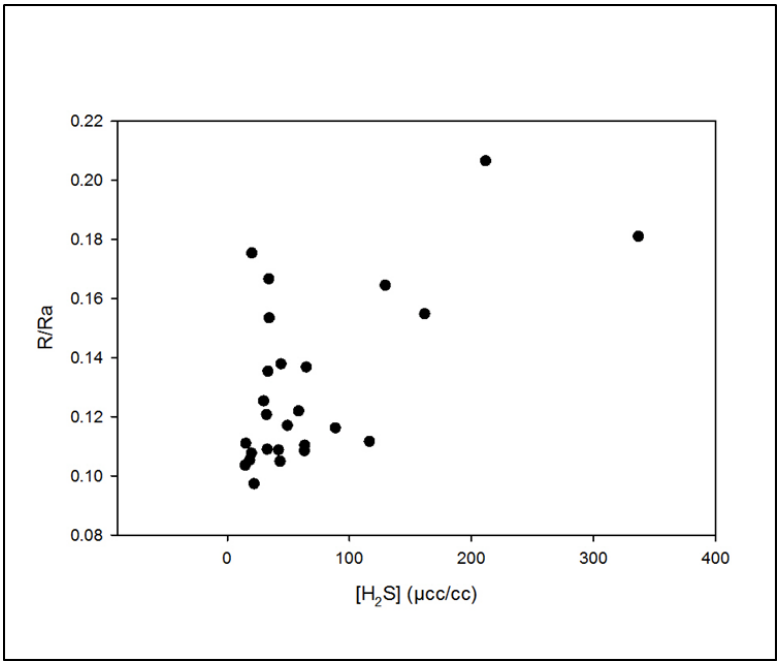


Figure 6. H_2S vs R/Ra plot. H_2S increases with increasing R/Ra, and thus, mantle-derived fluids. The mantle is not necessarily the source of H_2S, but provides the heat necessary for TSR.

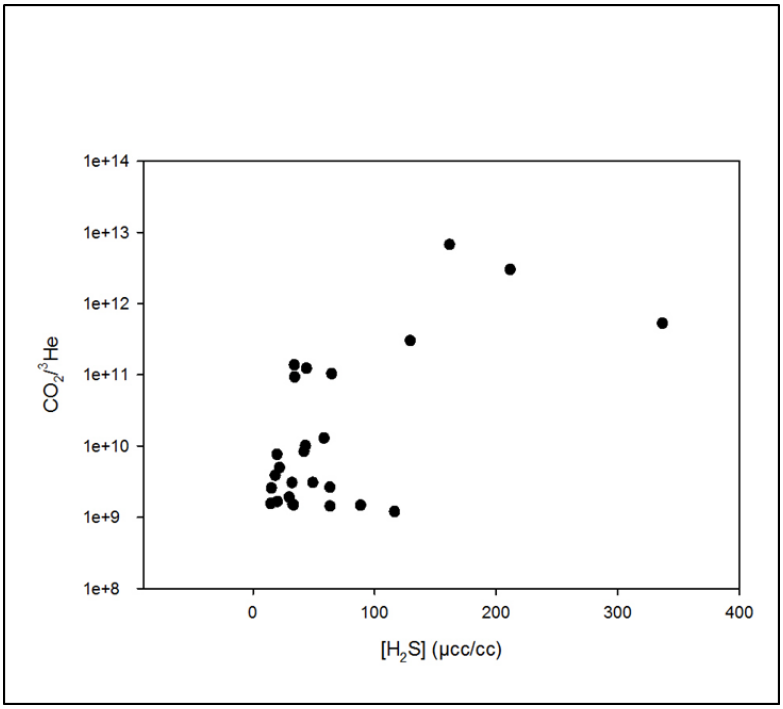


Figure 7. H_2S vs $CO_2/^3He$. Increasing [H_2S] is not a result of an increasing mantle component; otherwise this plot would show a negative correlation. The high CO_2 relative to ^3He is indicative of thermally-induced contributions brought to the system by way of higher temperature mantle fluids.

6.4 Noble Gases and Hydrocarbon Production

In addition to distinguishing the source of carbon dioxide and H_2S, noble gases may also provide valuable insight into important economic characteristics of hydrocarbon reservoirs. When fluids move in the subsurface either by natural geological processes or are released to

producing wells, the isotopes of noble gases fractionate according to their mass based on the relative size of the atom, which dictates individual solubility and diffusional constants. For example, during any style of fluid migration, He is preferentially concentrated in the migrating fluid, meaning that the fluid that has left the system becomes enriched in light components, while the residual fluids-in-place preferentially retain the heavier noble gases. As a result, comparing light noble gases to heavy ones allows us to determine how much fluid has left the system and how much remains today. This means that by measuring the relative amounts of isotopic fractionation one can determine the degree of open or closed system behavior a given system has experienced.

Darrah and Poreda (2013) found that fluids in unaltered black shales from diverse geological settings were found to have a $^{20}Ne/^{36}Ar$ value of approximately 0.10 to 0.15 and a $^{4}He/CH_4$ value of approximately 500, consistent with air-saturated water and thermogenic gas production, respectively. By comparison, hydrocarbon fluids that have migrated to overlying formations were enriched in $^{20}Ne/^{36}Ar$ (>0.8) and $^{4}He/CH_4$ (800), respectively. In the present study area, each of these ratios has a value well below the anticipated values for *in-situ* hydrocarbons, as evidenced by tight shale gases globally. Interestingly, some of the values for the Eagle Ford plot near zero (Figure 8). These lower values reflect either hydrocarbon loss during the early stages of hydrocarbon migration or hydrocarbon depletion during modern, anthropogenic oil and gas production.

Overall, the Eagle Ford Shale is a tight, closed system where fluids are being extracted via industry production, leaving behind fluids that are depleted of light noble gases such as ^{4}He and ^{20}Ne (Figures 9 and 10). From an individual well perspective, the extremely low values for the aforementioned ratios correspond to production nearing its end (i.e., low residual fluids-in-

place values). Hydrocarbons, water, and the associated noble gases have been removed in such a way that ***only*** the heaviest of the noble gases have yet to migrate. The CW 2, CP 4, CP 10, and JH12 wells have low methane, high $^{132}Xe/^{84}Kr$, high $CO_2/^3He$, and interestingly enough are on the higher end of the R/Ra spectrum within this sample population (Figure 11a and b). Surprisingly, these wells are not necessarily the oldest or longest producing wells. The JH12 well was the most recent to have been completed before sampling. These wells likely do not have much time left as useful producers, as evidenced by low initial production values on these well systems.

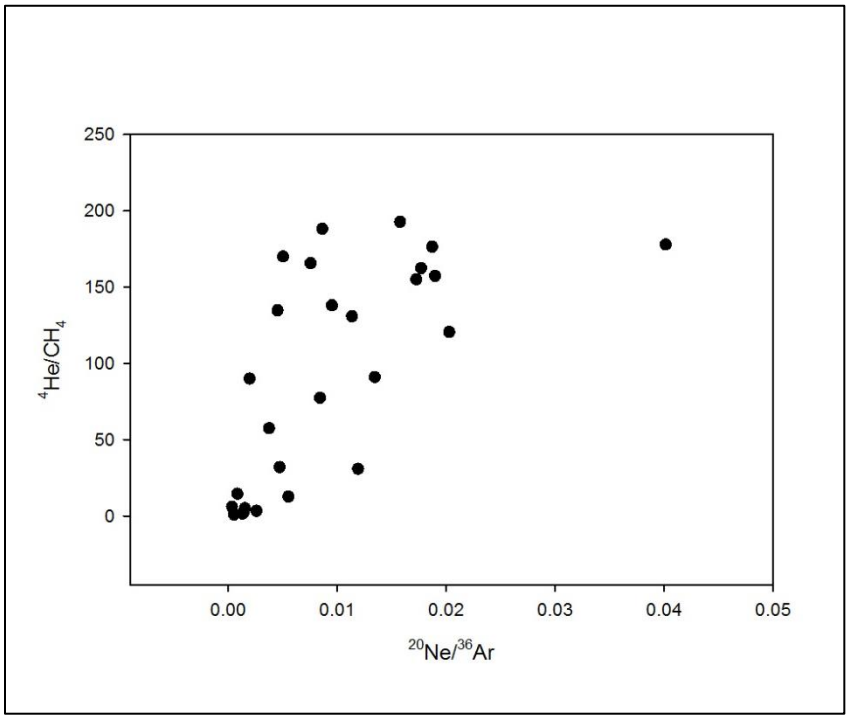


Figure 8. $^4He/CH_4$ vs $^{20}Ne/^{36}Ar$. The fractionation of fluid components can be used to determine the extent of migration into or out of a system. The data points in the lower left represent fluid-depleted zones, where nearly all of the light components (^4He, ^{20}Ne) have left via hydrocarbon production.

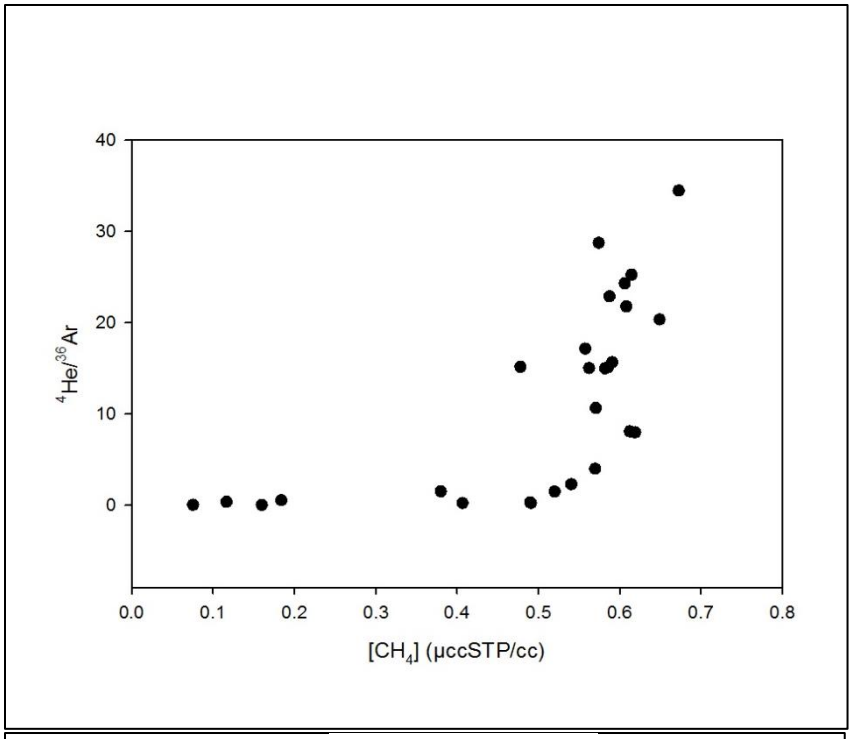


Figure 9.^{4}He/^{36}Ar vs [CH_4]. Elevated ^{4}He relative to ^{36}Ar is indicative of a system with little fluid loss. Methane, here, serves as a proxy for hydrocarbon production. Data points in the upper right represent wells with high production potentials while the ones in the lower left represent fluid-depleted wells.

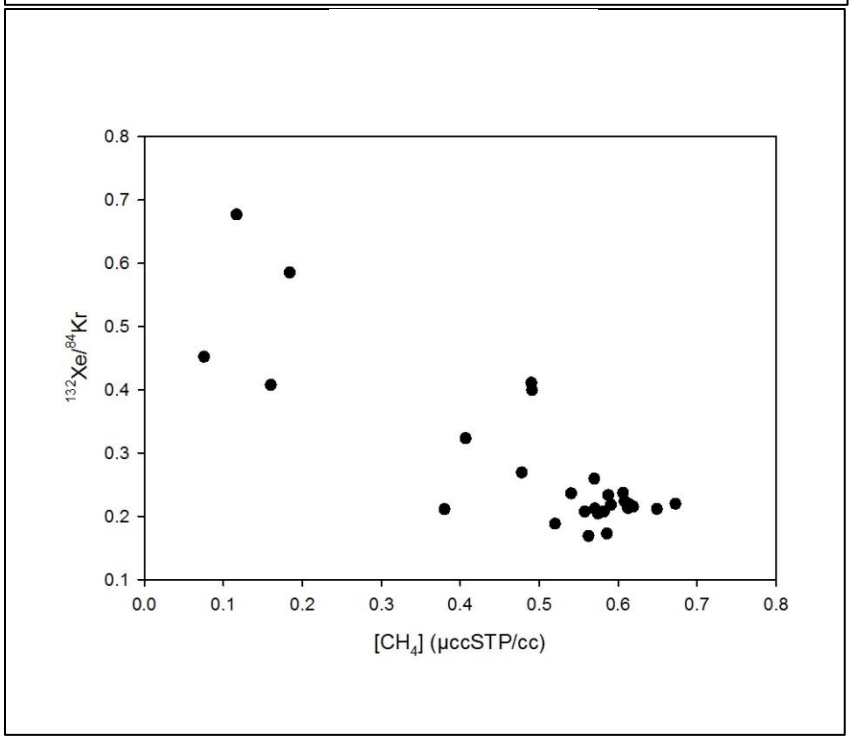
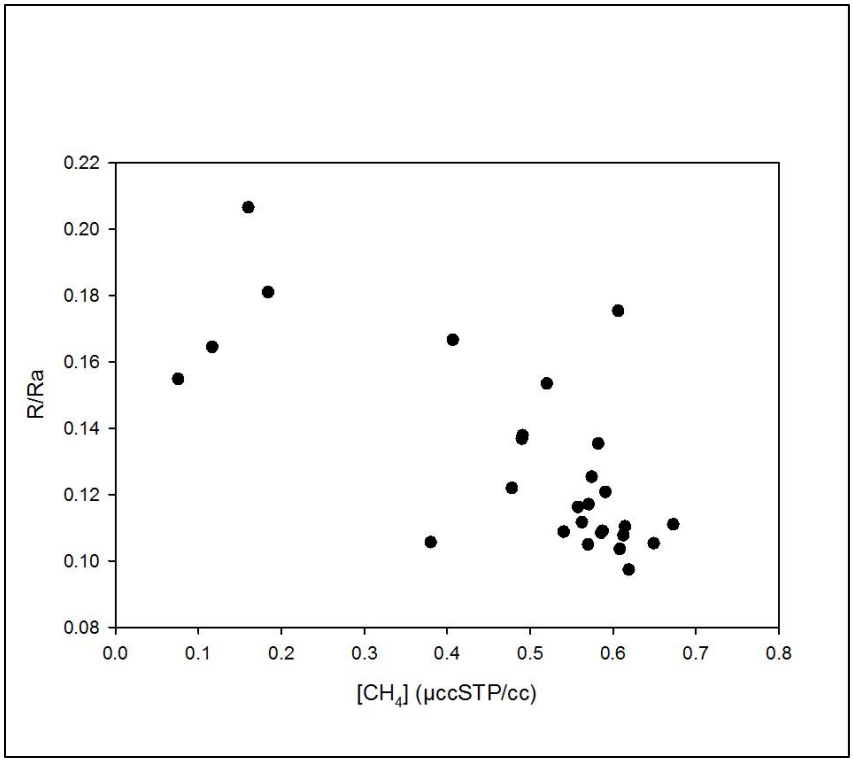


Figure 10. ^{132}Xe/^{84}Kr vs [CH_4]. ^{132}Xe is the last of the noble gases to leave a system via fractionation during migration processes. The up- and leftward trend shows wells with decreasing amount of fluids left in place.



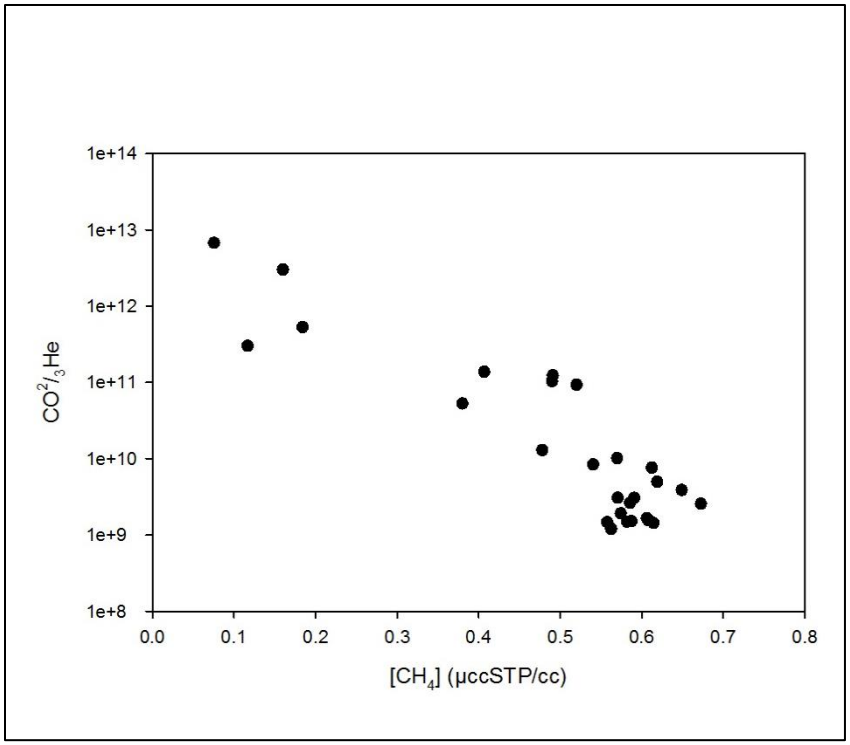


Figure 11. $CO_2/^3He$ vs $[CH_4]$ (top) and Figure 12 R/Ra vs $[CH_4]$ (bottom). Increasing CO_2 with decreasing methane would suggest the oxidation of methane, but in looking at the increasing R/Ra values for low methane, mantle-derived fluids play an important role in the addition of CO_2 while the location near normal faults provides migration pathways for hydrocarbons to leave, in addition to production.

7. Conclusions

The Eagle Ford Shale is a dynamic unit with a complex geologic history. Analysis of major and noble gas components of the oils and associated gases of this formation reveal a significant mantle component, with R/Ra values an order of magnitude higher than average crustal rocks. These mantle-enriched fluids also follow along the strike of the Charlotte Fault Zone, an ancient failed rift setting.

The rifting environment allowed for excess heat in this area of Eagle Ford Shale production, contributing to elevated CO_2 concentrations from a combination of mantle-derived fluids and thermally-altered carbonates. Similarly, elevated H_2S concentrations appear to be driven by thermochemical sulfate reduction following the emplacement of hydrothermal CO_2.

The fractionation of noble gases provides insight into reservoir quality for oil and gas production. The Eagle Ford Shale is a tight, closed system where a small amount of original fluids-in-place have been extracted. There are some individual wells, however, that do not have promising futures in terms of production as seen by elevated $^{132}Xe/^{84}Kr$ and depleted $^{20}Ne/^{36}Ar$ values.

8. Future Work

There are several steps forward with this project. The first of which is to complete the analysis of all collected samples. Secondly, More detailed contour maps of high H_2S areas need to be made to see if there is a stronger correlation with mantle contributions in the larger data set. Other future work could include collecting samples from elsewhere in the Eagle Ford Shale and other formations to see how the R/Ra values differ in an area without the extensional faulting regime seen so clearly in this study area.

Stable carbon isotope analyses have been done on a select number of the samples used in this project, but further studies can be done to determine the original isotopic composition of kerogen and to make inferences about the onset of oil and natural gas generation. Preliminary work has been done following the methods of Chung et al (1988).

Comparison of rifting and failed rift environments is an interesting direction in which this study could continue. In studies of the East African Rift, R/Ra values can exceed 10 (Darrah et al, 2013). The suspected failed rift in south Texas has gases with R/Ra values around 0.1. Future work could be done with different regions with known extensional regimes to determine whether or not there exists a particular R/Ra value that indicates a successful rift.

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